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The Interaction of Krypton and an Exfoliated Graphite at 77.4 K

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An exfoliated graphite sample was prepared having a significant increase in basal plane area over the original highly ordered pyrolytic graphite crystal. The boundary planes of the expanded sample appeared intact and were highly reflective. The krypton adsorption at 77.4 K was at first linear with p/p_0, then reached a plateau over the range from 0.45 to 0.65, and then increased uniformly to p/p_0 of 0.99, where p is pressure and p_0 is the sublimation vapor pressure of solid krypton. Each desorption branch initiated from several levels of adsorption decreased only slightly to the lowest pressures measured ($p/p_0 \sim 0.01$). A model is proposed in which the adsorption process is concomitant with a contraction between adjoining graphite lamellae.

1. INTRODUCTION

The dimensional changes that accompany gas-solid adsorption processes have been observed in many systems (1). The changes are readily measurable when the surface area of the solid is large. A factor of equal importance, however, is the particular structure of the solid since this determines the degree to which the structure can respond to the thrust of the interaction between gas and solid with a measurable displacement.

Graphite should be an excellent crystal with which to follow dimensional changes because of the small energy between the basal planes of the structure. The process of intercalation is related in part to the ready displacement of groups of these planes in particular chemical environments (2, 3). This paper is concerned with the unique krypton adsorption and desorption isotherms at 77.4 K obtained with an exfoliated sample of graphite derived from the intercalation product of a highly ordered pyrolytic graphite. A model is proposed wherein the adsorption data may be explained in terms of dimensional changes.

2. EXPERIMENTAL AND RESULTS

The sample of highly-ordered pyrolytic graphite was covered with a mixture of liquid bromine and nitromethane. After a contact time of several hours, the liquids were removed under vacuum with heating. The structure rapidly exfoliated at about 150°C. The initial dimensions of the graphite were $3\times5\times0.5$ mm and the final product increased in height to 50 mm in vacuum.

The composition of the original graphite was 100.0% C and 0.0% H; the exfoliated sample was 99.5 mole% C and 0.0% H as determined by combustion analysis. The residual in the latter can be attributed to bromine, in common with general experience reported for the intercalation of graphite by bromine (3). The X-ray diffraction of thin sections

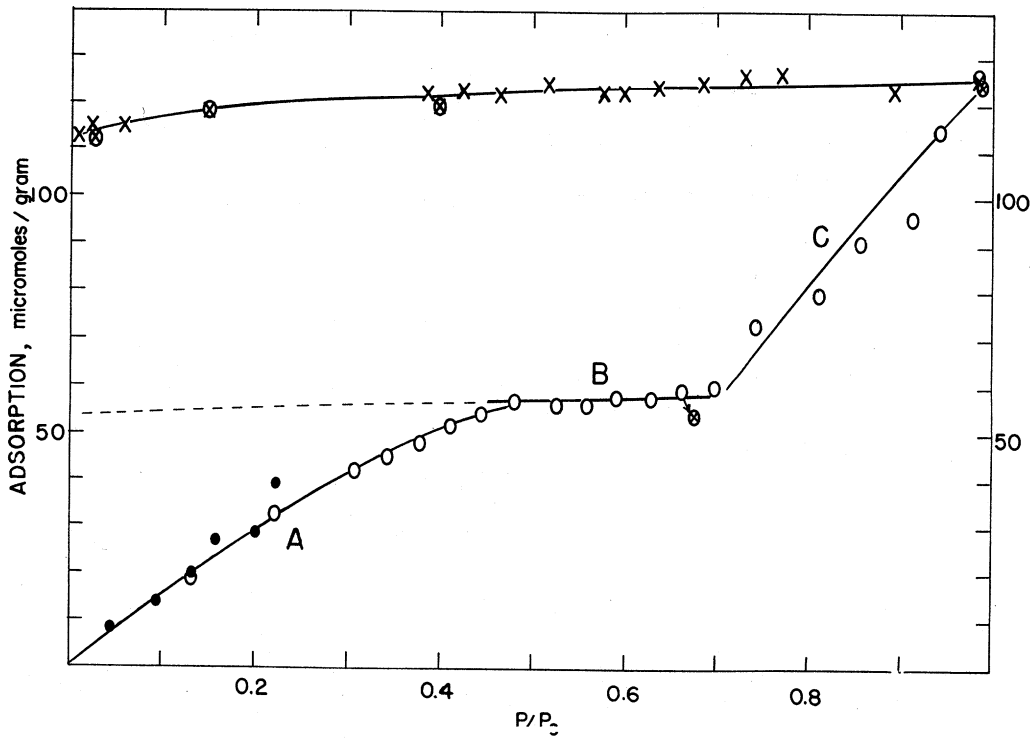

FIG. 1. The adsorption of krypton at 77.4 K on exfoliated graphite. Adsorption points are open and closed circles; desorption points are given by crosses; the extended contact times are given by crosses within circles.

placed horizontally on the crystal support of the diffractometer showed little difference in the 002 separation for the original and exfoliated graphites; the average value was 6.7012 Å.

The adsorption of krypton was determined volumetrically (4). The thermistor pressure element was calibrated against a McLeod gauge and the sample was protected from mercury vapor by an isolation trap (5) cooled with liquid nitrogen. Corrections were made for the thermodiffusion of krypton between 77.4 K and room temperature (6). The reproducibility of the pressure readings was ± 0.005 Torr and the amount adsorbed was known to a precision of $\pm 2\%$. The sample was heated in vacuum at 250°C before each isotherm except as noted.

The krypton isotherm in Fig. 1 is characterized by three regions. At pressures up to about $p/p_0 = 0.2$ [p is the observed pressure and p_0 is the sublimation vapor pressure of krypton at 77.4 K (8)] the adsorption branch, A, was nearly linear. The adsorption then gradually approached a plateau, B, that extended over the range p/p_0 of 0.45–0.65. With a further increase in pressure, the adsorption, C, increased approximately linearly to p/p_0 of 0.99, the highest pressure measured. The desorption branch, starting from p/p_0 of 0.99, defined a second plateau which decreased only slightly as the desorption was followed to the lowest measured pressure of $p/p_0 = 0.01$. The points indicated by a cross within a circle designate that a long period of time, usually overnight, had elapsed with the sample maintained at 77.4 K. The point at $p/p_0 = 0.99$ was contacted for three days. Upon extended contact times there was only a small variation for each measured point which indicated that the adsorption and desorption processes involved a series of steady states.

In a second series of measurements the

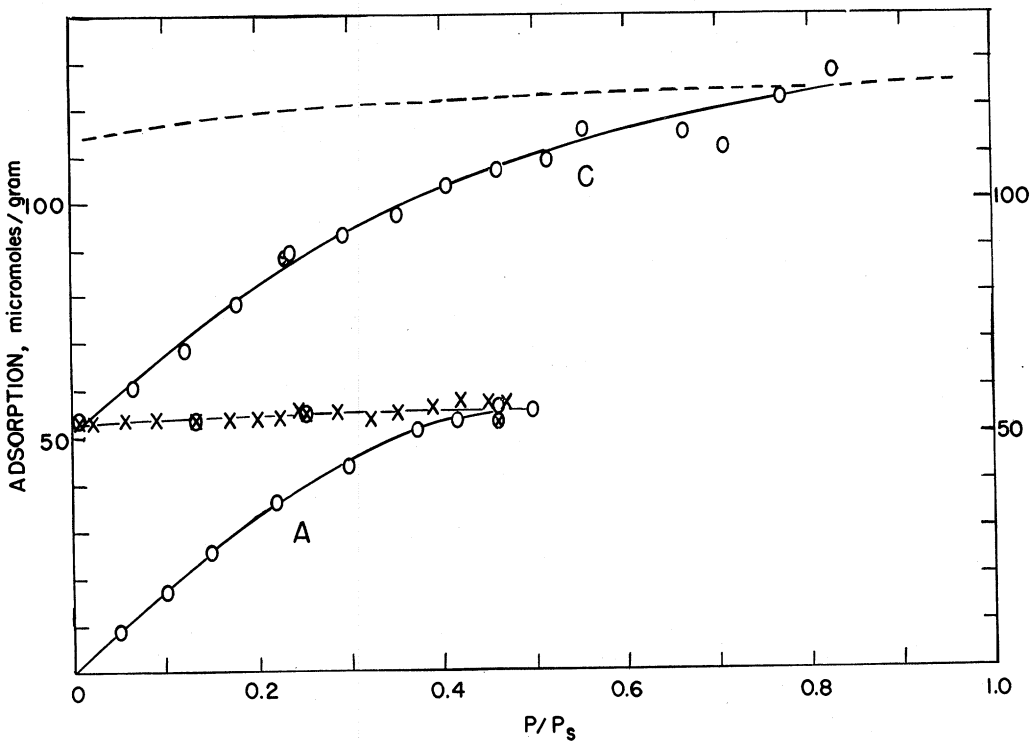

FIG. 2. Adsorption of krypton in region A and desorption initiated from the plateau B of Fig. 1.

adsorption (points ○ in Curve A of Fig. 2) was followed up to p/p_0 of 0.5 and then the desorption (points X) initiated. The desorption followed the plateau which only decreased slightly to the lowest measured pressure of 0.01. Three of the desorption points and one of the adsorption points designated by ⊗ correspond to overnight waiting preiods. Again the hysteresis loop did not close at p/p_0 of 0.01.

In two other experiments, the results shown in Fig. 3, the desorption was initiated from adsorption points before the first plateau was reached, viz. at p/p_0 of 0.34 and 0.16. Once more the desorption branches were also very nearly horizontal; the hysteresis branch did not close even at the lowest relative pressure measured ($p/p_0 = 0.02$).

Figure 2 also summarizes the results of an additional experiment. After the adsorption, A, had been followed by the desorption (points X) to a relative pressure of 0.01, the sample remained at this pressure for an overnight waiting period; the krypton retained amounted to 55 μmole/g. At this point additional krypton was introduced and the adsorption isotherm, Curve C, was determined. This increased uniformly and appeared to approach asymptotically the level of adsorption previously reported in Fig. 1. One of the points ($p/p_0 = 0.24$) on Curve C was held for a waiting period of 18 hr without appreciable change. The experiment is somewhat analogous to the reported adsorption behavior of iron catalysts for carbon monoxide at 90 K. Emmett and Brunauer (9) showed that the carbon monoxide was physically adsorbed on a previously irreversibly adsorbed layer of carbon monoxide which could not be removed by desorption at −73°C.

4. DISCUSSION

The adsorption isotherms reported in Figs. 1, 2 and 3 are not typical of the conventional physical adsorption of krypton at 77.4 K; also

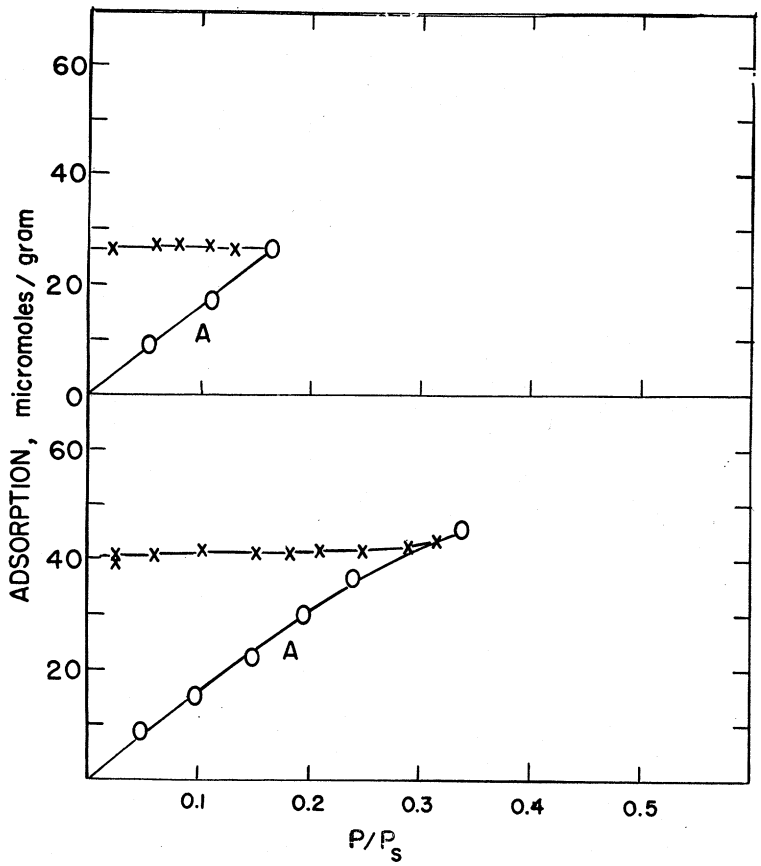

FIG. 3. Adsorption of krypton and the desorptions initiated from locations before the plateau B of Fig. 1.

the desorption isotherms describe a hysteresis behavior that is most unusual. Recently, Fuller, Holmes, Gammage, and Becker (10) reported almost linear adsorption isotherms for argon and oxygen on a sample of lunar soil at 77.1 K, but unlike the present results, they found the isotherms to be reversible.

The presence of lamella compounds between the basal planes of graphite and adsorbed krypton is indicated by the almost pressure-independent desorption from any one of a number of adsorption points. For example, the plateau from p/p_0 of 0.45 to 0.65 (Fig. 1) is approximately 60 μmole Kr/g of graphite. Consider each lamella as a rectangular parallelepiped of total basal plane area A (cm^2) and thickness d (cm). Using 2.25 g/cm^3 for the density of graphite, $A = 0.888/d$. The area occupied by a carbon atom in the basal plane is 2.619×10^{-16} cm^2. If $d = 1000$ Å, as suggested by electron microscopy, then $C/Kr = 9$ which is equivalent to C_9Kr. If one considers, however, that each Kr layer is between two basal planes, then C/Kr is 18. Hence, the plateau observed in the range of p/p_0 0.45 to 0.65 corresponds to $C_{18}Kr$ and that formed upon desorption from p/p_0 of 0.99 is equivalent to C_9Kr. The area occupied by one Kr atom would then be 23.5 Å^2, in substantial agreement with other reported values. There is a direct dependence of the stoichiometry of the lamella adsorption complex on the thickness of the lamellae, d. For instance, a value of $d = 1200$ leads to C_8Kr and the area of an adsorbed Kr atom would then be 21 Å^2 (11).

The energy of adsorption of a krypton atom

approaching the basal plane of graphite along a reaction path either directly over a carbon atom or over the center of the hexagon is about 2800 cal/mole (12, 13). This energy is equivalent to 7.03×10^6 ergs per indicated monolayer for the exfoliated graphite (60 μmole/g). When two planes of separate lamellae are within the potential field of a Kr atom, the total energy may be approximately twice this value. The total surface energy at the graphite/air interface has been reported to be close to 120 ergs/cm^2 for the basal plane (14), or $120 \times 7.2 \times 10^4 = 8.6 \times 10^6$ ergs for the energy of the sample of exfoliated graphite. Thus, it may be possible for the energy of adsorption to exceed the energy of the exfoliated graphite and thus permit the type of hysteresis observed.

The krypton adsorption appears to be critically dependent on the intercalation process itself. A number of pressure independent compositions have been reported during intercalation. Hooley and Bartlett (15) prepared C_7FeCl_3 and $C_{12}FeCl_3$ at 300°C. The recent work of Thomy (16) and Thomy and Duval (17), who prepared C_8FeCl_3 (using $FeCl_3$ vapor at 320°C and graphite at 300°C), is pertinent to the present investigation. The $FeCl_3$ was expelled from the various samples by thermal decomposition at 900–1500°C and several different exfoliated graphite structures were obtained. Their adsorption isotherms of krypton, xenon, and methane were characterized by four vertical rises, those for krypton were located at p/p_0 of 0.38, 0.77, 0.92, and 0.97. A fact of significance to the present investigation is that Thomy and Duval found no evidence of hysteresis. The stability of the exfoliated graphites of Thomy and Duval appears to be greater than the samples used in the present investigation. This stability between lamellae is apparently suffciently large to give reversible adsorption–desorption isotherms. However, it may be possible that the sharp rises observed by Thomy and Duval may be due to reversible slippage or tilts in the structure enlarging the lamellar separation. This may be a factor in the several two-dimensional phase transitions proposed by Thomy and Duval for the adsorbed layer.

It does not appear possible to explain the observed desorption hysteresis using a model based on conventional capillary condensation in a rigid solid structure. The nearly horizontal desorption isotherm of the expanded graphite indicates that the krypton may be held strongly in the potential field of the graphite lamellae when the desorption is initiated from any level of adsorption. Such behavior requires that a consideration be given to the detailed macrostructure of the graphite in which dislocations and slip planes exist at the boundaries joining lamellae. A great deal of careful experimental work is required to further our understanding of these new and most interesting phenomena.

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